

1a

PATENT SPECIFICATION

(11) 1 535 826

1 535 826

- (21) Application No. 6752/76
- (22) Filed 20 Feb. 1976
- (31) Convention Application No. 2507461
- (32) Filed 21 Feb. 1975 in
- (33) Federal Republic of Germany (DE)
- (44) Complete Specification published 13 Dec. 1978
- (51) INT CL² C07C 47/19//31/18 47/20
- (52) Index at acceptance

C2C 200 20Y 248 30Y 350 360 361 36Y 382 43X 507 509 50Y
54X 569 633 643 65Y 66Y TH TJ YP

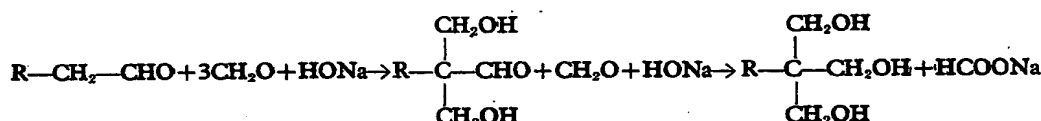


(54) MANUFACTURE OF α,α -DIMETHYLOL-SUBSTITUTED ALIPHATIC ALDEHYDES

(71) We, BASF AKTIENGESSELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to a process for the manufacture of α,α -dimethylol-substituted aliphatic aldehydes by reaction of an aldehyde with formaldehyde in the presence of a base.

German Printed Application 1,154,080 discloses the reaction of aldehydes, containing at least 3 carbon atoms and containing 2 hydrogen atoms in the α -position, with formaldehyde in the presence of basic compounds, e.g. alkali metal hydroxides or alkaline earth metal hydroxides, to give trimethylolalkanes. The reaction can be represented by the following equation:



In this reaction, dimethylolaldehydes are formed as transient intermediates, which react with formaldehyde and the base, in a Cannizzaro reaction, to give trimethylol compounds and a formate. The disadvantage of this process is that at least stoichiometric amounts of formates are formed as by-products. Because of the fact that they cause decomposition, the salts must be removed completely before the trimethylol compounds are purified by distillation, and these salts are a serious environmental problem, particularly in large-scale production. It is not possible to manufacture pure dimethylolaldehydes satisfactorily by this method, since substantial amounts of formaldehyde undergo a Cannizzaro reaction with the alkanal in the presence of the basic catalyst, and mixtures of components which are difficult to separate are formed.

German Published Application 1,952,738 discloses the use of lower tertiary organic amines as catalysts for the reaction of n-butyraldehyde with formaldehyde. In the examples, the use of trimethylamine and triethylamine is illustrated. In the description, only these two compounds are mentioned individually; from the statements made (page 3, 1st paragraph) it is merely possible to assume that straight chain trialkylamines, preferably with identical alkyl radicals, can be used. In this process, again, the formation of formates is neither avoided nor reduced. The advantage that the salt is more easily removable is counter-balanced by the increased effort required to regenerate the base. The process is unsatisfactory in respect of yield and purity of the products.

U.S. Patent 3,077,500 discloses the reaction of aldehydes in the presence of tertiary amines and a basic anion exchanger, to give corresponding aldols; the patent teaches that, as a rule, the amine serves to maintain the catalytic activity of the exchanger resin. In the absence of the exchanger, the catalytic action of the amine alone is less; the conjoint use of the amine and the exchanger is emphasized particularly for the case of reactions carried out at atmospheric pressure. The process can also be carried out in the absence of the amine. All the amines mentioned in the description are straight-chain amines and the examples only illustrate the use of

BEST AVAILABLE COPY

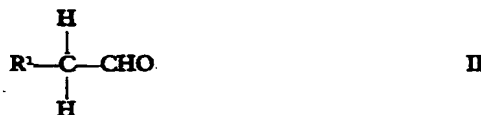
trimethylamine and triethylamine. The examples further show that amines without the exchanger are only used in the case of the auto-condensation of a single aldehyde or of the condensation of formaldehyde with a ketone. Thus, e.g., the patent teaches that triethylamine brings about the auto-condensation of butyraldehyde (Example 9). Examples 10 and 11 show that with formaldehyde only one methylol group is condensed onto acetone or onto methyl ethyl ketone in the presence of triethylamine and in the absence of exchangers, even though there are other hydrogen atoms in the α -position to the carbonyl group and therefore further condensation would be possible.

In the reaction of aldehydes, containing 2 hydrogen atoms in the α -position, with formaldehyde, equilibria exist between the possible aldol-forming reactions and side reactions, e.g. elimination of water in the α,β -positions; in addition to the end products, a range of other products, in some cases of higher molecular weight, e.g. aldols and ether aldehydes, are formed. Hydrogenation of the reaction mixture gives trimethylol compounds contained in heterogeneous mixtures, from which they are difficult to isolate.

We have found that an advantageous method of obtaining an α,α -dimethylol-substituted aliphatic aldehyde of the formula



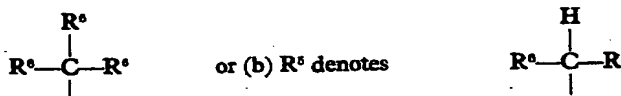
where R^1 is an aliphatic radical, by reaction of an aldehyde with formaldehyde in the presence of a base, is to react an aldehyde of the formula



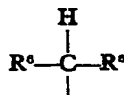
where R^1 has the above meaning, with formaldehyde in the presence of a tertiary amine catalyst of the formula



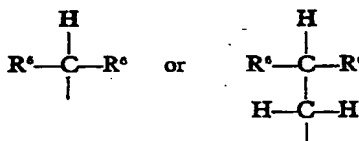
where R^2 and R^3 separately are identical or different aliphatic radicals, or together form with the linking nitrogen atom a heterocyclic ring and R^4 and R^5 are identical or different aliphatic radicals, and in addition R^4 may denote hydrogen if (a) R^5 denotes



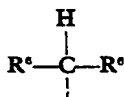
and R^2+R^3 +the linking N atom form a heterocyclic ring or (c) R^5 denotes



and R^2 denotes

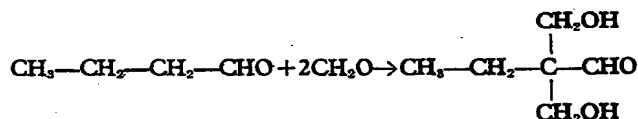


and (ii) R⁵ may denote hydrogen if (a) R²+R³+ the linking N atom form a heterocyclic ring and R⁴ denotes an aliphatic radical or (b) R⁴ denotes an aliphatic radical and R² denotes



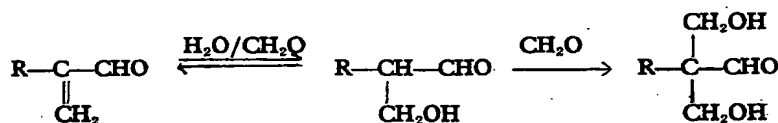
5 R⁶ throughout denoting an aliphatic radical and individual radicals R⁶ and individual radicals R⁴ being identical or different. 5

When n-butyraldehyde is used, the reaction can be represented by the following equation:



10 Compared to the conventional process, the process according to the invention is able to give α,α -dimethylol-substituted aliphatic aldehydes more economically and more simply, in most cases in better yield, and in higher purity. In view of the purification operations required in the conventional processes the process of the invention generally gives a higher space-time yield of the overall operation, particularly on an industrial scale. The formation of by-products is substantially reduced and mixtures containing by-products which are difficult to remove are not formed to a substantial degree. By-products formed are small amounts of the corresponding α -substituted acrolein and α -substituted alkenal as well as trimethylol-substituted aliphatic compound and N,N,N-trisubstituted ammonium formates. 15

20 Surprisingly, the formation of α -substituted acroleins is reversible under the conditions according to the invention; reaction of the acrolein with water and formaldehyde in the presence of the amine III gives α,α -dimethylol-substituted aliphatic aldehyde via α -monomethylol-substituted aliphatic aldehyde: 20



25 The α -substituted acroleins, which are the most important by-products formed, can thus be converted together with the dimethylol aldehydes, e.g. by hydrogenation, to industrially valuable α -substituted alkanols, or can be recycled to the synthesis of the dimethylol aldehyde. Trisubstituted ammonium formates can be isolated by distillation if their boiling point is sufficiently low, but when a trimethylol compound is to be produced, the said formates can, without disadvantage, be introduced into the hydrogenation reactor together with the dimethylolaldehyde, and as a rule undergo an advantageous degradation, with liberation of the tert-amine III. Thus, a further advantage of the process according to the invention compared to the conventional processes is that the by-products formed can be removed easily and can be converted into industrially useful products. All these advantageous results are surprising in the light of the prior art. In the light of U.S. Patent 3,077,500, low yields, or at least poorer yields of end product, and the formation of heterogeneous mixtures containing aldols formed by auto-condensation of the aldehyde, and monomethylol compounds, would have been expected. It is especially surprising that particularly the branched alkylamines used according to the invention are exceptionally selective catalysts for the reaction according to the invention. 30

35 The starting materials II are reacted with a stoichiometric amount or an excess of formaldehyde, preferably using a molar ratio of from 1 to 8 moles, and especially 2 to 4 moles, of formaldehyde per mole of starting material II. Preferred starting materials II and accordingly preferred end products I are those where R¹ is linear alkyl of 1 to 6 carbon atoms. The above alkyl radicals can further be substituted by groups which are inert under the reaction conditions, e.g. alkyl or alkoxy, each of 1 to 3 carbon atoms. 40

45 45

Examples of suitable starting materials II are 3-ethyl-, 3-n-propyl-, 3-isopropyl-, 3-n-butyl-, 3-isobutyl-, 3-sec.-butyl-, 3-tert.-butyl-, butanal and corresponding -n-pentanal, -n-hexanal and -n-heptanal; 4-ethyl-, 4-n-propyl-, 4-isopropyl-, 4-n-butyl-, 4-isobutyl-, 4-sec.-butyl-, and 4-tert.-butyl-pentanal, -n-hexanal and -n-heptanal; 5-ethyl-, 5-n-propyl-, 5-isopropyl-, 5-n-butyl-, 5-isobutyl-, 5-sec.-butyl- and 5-tert.-butyl-n-hexanal and -n-heptanal; 3-methyl-hexanal and 3-methyl-heptanal; 4-methyl-pentanal, 4-methyl-heptanal, 5-methyl-hexanal and 5-methyl-heptanal; 3,3,5-trimethyl-n-pentyl-, 3,3-diethylpentyl-, 4,4-diethylpentyl-, 3,3-dimethyl-n-butyl-, 3,3-dimethyl-n-pentyl-, 5,5-dimethylheptyl-, 3,3-dimethylheptyl-, 3,3,4-trimethylpentyl-, 3,4-dimethylheptyl-, 3,5-dimethylheptyl-, 4,4-dimethylheptyl-, 3,3-diethylhexyl-, 4,4-dimethylhexyl-, 4,5-dimethylhexyl-, 3,4-dimethylhexyl-, 3,5-dimethylhexyl-, 3,3-dimethylhexyl-, 3,4-diethylhexyl-, 3-methyl-4-ethylpentyl-, 3-methyl-4-ethylhexyl-, 3,3,4-trimethylpentyl-, 3,4,4-trimethylpentyl-, 3,3,4-trimethylhexyl-, 3,4,4-trimethylhexyl- and 3,3,4,4-tetramethylpentyl- aldehyde; propanal, n-butanal, n-pentanal, 3-methylbutanal, n-hexanal, 3-methylpentanal, n-heptanal, 4-methyl-hexanal and n-octanal are preferred.

The reaction is in general carried out at from 15 to 120°C, preferably from 30 to 90°C and especially from 40 to 85°C, under reduced pressure, superatmospheric pressure or atmospheric pressure, preferably the latter, and batchwise or continuously. In general, water is used as the reaction medium, in most cases in the form of an aqueous formaldehyde solution, preferably containing from 20 to 40 percent by weight of formaldehyde. In total, the amount of water used can be from 20 to 80% by weight, advantageously from 40 to 60% by weight, based on total starting mixture. If desired, an organic solvent which is inert under the reaction conditions and preferably is readily miscible with water may also be present; advantageous solvents are cyclic ethers, e.g. tetrahydrofuran and dioxane, esters, e.g. methyl acetate, ethyl acetate and methyl propionate, and alkanols, e.g. ethanol, methanol, glycol, ethylene glycol monoethyl ether and methylglycol. Suitable amounts of solvent to use are from 50 to 1,000% by weight, preferably from 50 to 200% by weight, based on starting material II.

Suitable amounts of catalyst III are from 0.03 to 0.15 mole, especially from 0.05 to 0.1 mole, per mole of starting material II. It is advantageous if the catalyst has a boiling point below that of the dimethylolalkanal II. Preferred tertiary amines are those defined above of the formula III where any aliphatic radical R², R³, R⁴, R⁵ or R⁶ is alkyl of 1 to 7 carbon atoms, more preferably of 1 to 5 carbon atoms in the case of R² and R³ and of 1 to 3 carbon atoms in the case of R⁴, R⁵ and R⁶, optionally substituted by one or more dialkylamino groups and/or hydroxyl groups, preferably by one dialkylamino group or one hydroxyl group, preferably in the ω-position, the alkyl groups of any dialkylamino groups being identical or different and each being of 1 to 5 carbon atoms, and where any heterocyclic ring formed by R² and R³ and the linking nitrogen atom has 5 or 6 ring members, which may include a further nitrogen atom or an oxygen atom, and may further be substituted by one or more groups which are inert under the reaction conditions, e.g. alkyl or alkoxy groups each of 1 to 3 carbon atoms, dialkylamino groups each of 1 to 3 carbon atoms per alkyl, and hydroxyl groups.

Examples of suitable catalysts III are N,N-di-(methyl)-, N,N-di-(ethyl)-, N,N-di-(n-propyl)-, N,N-di-(isopropyl)-, N,N-di-(n-butyl)-, N,N-di-(isobutyl)-, N,N-di-(sec.-butyl)-, N,N-di-(tert.-butyl)-, N,N-di-(n-pentyl)-, N,N-di-(pentyl-2)-, N,N-di-(pentyl-3)-, N,N-di-(n-hexyl)-, N,N-di-(n-heptyl)-, N,N-di-(n-octyl)-, N,N-di-(n-nonyl)-, N,N-di-(n-decyl)-, N,N-di-(2-ethylhexyl)-, N,N-di-(2,2,6-trimethyl-n-pentyl)-, N,N-di-(2-ethylpentyl)-, N,N-di-(3-ethylpentyl)-, N,N-di-(2,3-dimethyl-n-butyl)-, N,N-di-(2,2-dimethyl-n-butyl)-, N,N-di-(2-methylpentyl)-, N,N-di-(3-methylpentyl)-, N,N-di-(2,2,4-trimethylpentyl)-, N,N-di-(2-methylheptyl)-, N,N-di-(3-methylheptyl)-, N,N-di-(4-methylheptyl)-, N,N-di-(3-ethylhexyl)-, N,N-di-(2,2-dimethylhexyl)-, N,N-di-(2,3-dimethylhexyl)-, N,N-di-(2,4-dimethylhexyl)-, N,N-di-(2,5-dimethylhexyl)-, N,N-di-(3,3-dimethylhexyl)-, N,N-di-(3,4-dimethylhexyl)-, N,N-di-(2-methyl-3-ethylpentyl)-, N,N-di-(3-methyl-3-ethylpentyl)-, N,N-di-(2,2,3-trimethylpentyl)-, N,N-di-(2,2,4-trimethylpentyl)-, N,N-di-(2,3,3-trimethylpentyl)-, N,N-di-(2,3,4-trimethylpentyl)- and N,N-di-(2,2,3,3-tetramethylbutyl)-neopentylamine; corresponding amines with 2 of the above radicals which however differ from one another, e.g. N-methyl-N-ethyl-neopentylamine; 1,1-dimethyl-, 1,1-diethyl-, 1,1-di-n-propyl-, 1,1-diisopropyl-, 1,1-di-n-butyl-, 1,1-diisobutyl-, 1,1-di-sec.-butyl- and 1,1-di-tert.-butylethylamines having substituents R² and R³ on the nitrogen atom corresponding to those on the neopentyl-dialkylamines mentioned above; n-propylamines, isopropylamines, n-butylamines, isobutylamines, sec.-butylamines and tert.-butylamines as far as possible cor-

respondingly substituted in the 1-position of the alkyl radical and also correspondingly disubstituted on the nitrogen atom; N-(1,1-dimethyl-ethyl)-, N-(1,1-diethyl-ethyl)-, N-(1,1-di-n-propyl-ethyl)-, N-(1,1-diisopropyl-ethyl)-, N-(1,1-di-n-butyl-ethyl)-, N-(1,1-diisobutyl-ethyl)-, N-(1,1-di-sec-butyl-ethyl)- and N-(1,1-di-tert-butyl-ethyl)-pyrrolidines as well as N-n-propyl-, N-isopropyl-, N-n-butyl-, N-isobutyl-, N-sec-butyl- and N-tert-butyl-pyrrolidines as far as possible correspondingly substituted in the 1-position of the alkyl radical; piperidines, N'-methylpiperazines and morpholines substituted analogously to the above pyrrolidines, and analogous piperazines substituted at the 2nd nitrogen atom by the ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl group, N-neopentyl-pyrrolidine, N-neopentyl-piperidine, N-neopentyl-N'-methyl-piperazine, N-neopentyl-morpholine and analogous piperazine substituted at the 2nd nitrogen atom by the ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl group; 2,2-diethyl-, 2,2-di-n-propyl-, 2,2-diisopropyl-, 2,2-di-n-butyl-, 2,2-diisobutyl-, 2,2-di-sec-butyl- and 2,2-di-tert-butyl-n-propyl-dialkylamines and -heterocyclics corresponding to the above N-neopentyl-dialkylamines and N-neopentyl-heterocyclics, as well as the analogously substituted 2,2-dimethyl-, 2,2-diethyl-, 2,2-di-n-propyl-, 2,2-diisopropyl-, 2,2-di-n-butyl-, 2,2-diisobutyl-, 2,2-di-sec-butyl- and 2,2-di-tert-butyl-n-butyl compounds and -ethyl compounds, and n-butyl compounds which are disubstituted by the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl group both in the 2-position and in the 3-position; isopropyl-pyrrolidine, sec-butyl-pyrrolidine and analogously substituted piperidines, N'-methyl-piperazines, morpholines and piperazines which are analogously substituted at the 2nd nitrogen atom by the ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl or tert-butyl group; monoalkylamines, substituted correspondingly to the above N-neopentyl-dialkylamines, which in place of the neopentyl group and an alkyl group carry 2 isopropyl groups or 2 isobutyl groups or 2 isopropyl groups which are substituted in the 1-position, or in the 1-position and at the same time in one or both of the ω -positions, by, in each case, 2 methyl, 2 ethyl, 2 n-propyl, 2 isopropyl, 2 n-butyl, 2 isobutyl, 2 sec-butyl or 2 tert-butyl groups, or 2 isobutyl groups which are substituted in one or both of the ω -positions by, in each case, 2 methyl, 2 ethyl, 2 n-propyl, 2 isopropyl, 2 n-butyl, 2 isobutyl, 2 sec-butyl or 2 tert-butyl groups; and corresponding tertiary amines which carry a hydroxyl group, or a dimethylamino, diethylamino, di-n-propylamino, diisopropylamino, di-n-butylamino, diisobutylamino, di-sec-butylamino or di-tert-butylamino group in the ω -position of 1 or 2 or all alkyl groups.

Preferred catalysts III are dimethylamino-neopentanol, 3-dimethylamino-2-methyl-2-propyl-propanol, 2,2-dimethyl-N,N'-tetramethyl-1,3-propylenediamine, pyrrolidino-neopentanol, 1-dimethylamino-neopentane, 1-dimethylamino-2,2-dimethylolpropane, 1-dimethylamino-2,2-dimethylolbutane, methyl-diisobutylamine, ethyl-diisopropylamine, propyl-diisopropylamine, triisopropylamine, triisobutylamine, propyl-diisobutylamine, n-butyl-diisobutylamine, N-isopropyl-pyrrolidine, N-isobutyl-pyrrolidine, N-isopropyl-piperidine, N-isobutyl-piperidine, methyl-ethylamino-neopentanol, diethylamino-neopentanol, piperidino-neopentanol, 3-(methyl-ethylamino)-2-methyl-2-propyl-propanol, 3-pyrrolidino-2-methyl-2-propyl-propanol, 3-piperidino-2-methyl-2-propyl-propanol, 3-dimethylamino-2-ethyl-2-butyl-propanol, 1-pyrrolidino-2,2-dimethylolpropane, 1-(methyl-ethylamino)-2,2-dimethylolpropane, 1,3-bis-[dimethylamino]-neopentane, 1,3-bis-[dimethylamino]-2,2-dimethylpropanol, methyl-ethylamino-neopentane, ethyl-diisobutylamine, butyl-diisopropylamine, tert-butyl-diisopropylamine, N-isopropyl-morpholine, N,N'-diisopropyl-piperazine, N-isobutyl-morpholine, N,N'-diisobutyl-piperazine, N-tert-butyl-pyrrolidine, N-tert-butyl-piperidine and N-tert-butyl-morpholine.

The reaction can be carried out as follows: a mixture of starting material II, formaldehyde, water and catalyst, if appropriate together with solvent, is kept at the reaction temperature for from 10 to 240 minutes, preferably from 15 to 60 minutes. The end product is then isolated from the reaction mixture in the usual manner, for example by distillation. An advantageous method of batchwise operation is to introduce the catalyst into the mixture of the starting materials, whilst this mixture is stirred within the stated temperature range, at a rate such that the heat of reaction can suitably be removed by cooling. It is also possible to take the aldehyde II and add formaldehyde and amine III conjointly thereto. For continuous operation, it is possible to use, e.g., a packed reaction tube or a stirred kettle cascade. The dimethylol-aldehyde product I can be isolated from the reaction product by stripping off any excess formaldehyde and distilling off the solvent, the catalyst and the lower-boiling by-products, the dimethylol aldehyde being left as the residue; alternatively, the dimethylol aldehyde can be subjected to further conversion, e.g. hydrogenation, directly

in the reaction mixture. The term "stripping" is used to denote purifying a material by removing another material in the form of a vapor mixture, e.g. the distillation vapor, in accordance with the definition in "Introduction to Chemical Engineering" by W. L. Badger and J. T. Banchero (McGraw-Hill Book Co. Inc. 1955), page 437, last paragraph. Surprisingly, dimethylolaldehydes I where R¹ is alkyl of 1 to 4 carbon atoms, i.e. up to 2,2-dimethylolhexanal, in the form produced according to the invention, can be distilled substantially without decomposition, and purified, on thin film evaporators at below 200°C, under reduced pressure. Whilst in all conventional processes a similar distillation of the desired dimethylol aldehyde I leaves residues and gives a distillate which is not a single substance, the end products I manufactured according to the invention as a rule leave less than 3% by weight of residues and thus give a purer dimethylol aldehyde. As may be seen from the Examples, the end products I manufactured in this way can be hydrogenated to trimethylol compounds R¹-C(CH₂OH)₃ simply and in accordance with conventional methods.

The dimethylol aldehydes I which may be manufactured by the process of the invention are valuable intermediates for the manufacture of trimethylol compounds, e.g. 1-trimethylolethane and 1-trimethylolpropane, which are industrially important components of polyurethane resins, alkyd resins, drying oils and plasticizers. They are, furthermore, starting materials for dimethylolcarboxylic acids, e.g. dimethylolpropionic acid and dimethylolbutyric acid, for dyes and for pesticides. Regarding their uses, reference may be made to the publications mentioned above and to Ullmanns Encyklopädie der technischen Chemie, Volume 3, pages 295 to 298.

In the Examples, parts are by weight.

EXAMPLE 1

26 parts of dimethylaminoneopentanol are added in the course of 10 minutes to a mixture of 488 parts of 37 per cent strength by weight formaldehyde and 144 parts of n-butyraldehyde whilst stirring at from 20 to 70°C. The reaction mixture is then stirred for a further 20 minutes at 78°C under reflux. The formaldehyde content is lowered to 0.05% by weight (based on the mixture) by stripping with steam, and the water and low-boiling constituents are removed by distillation, using a Sambay evaporator, at from 135 to 140°C and 10 mm Hg. 223 parts of crude dimethylolbutanal, corresponding to a yield of 84.5% of theory, based on n-butyraldehyde employed, are left as the residue. Distillation at 170°C and 2 mm Hg gives 212 parts of pure end product (80.3% of theory) of boiling point 133°C at 1 mm Hg.

Continuous catalytic hydrogenation of the pure end product in tetrahydrofuran (25 percent strength solution) at 110°C and 250 bars pressure of H₂, over a fixed bed hydrogenation catalyst consisting of 68% by weight of CuO, 6.4% by weight of Mn₂O₄, 3.6% by weight of MoO₃, and 3% by weight of H₃PO₄ (3 mm diameter catalyst extrudates), and fractional distillation, gives 199 parts of trimethylolpropane of boiling point 151°C at 1—2 mm Hg (melting point 53°C), corresponding to 92.4% of theory, based on pure end product, or 74.3% of theory, based on n-butyraldehyde employed.

COMPARATIVE EXAMPLES 2 AND 3

By way of comparison with Example 1, 488 parts of 37 per cent strength by weight formaldehyde and 144 parts of n-butyraldehyde are reacted with the aid of catalysts K at temperatures T, using the processes shown in the Table. Working up analogously to Example 1 gives crude dimethylolbutanal (CD) in yields of A₁% of theory, or pure end product (DMB) in yields of A₂% of theory, based on n-butyraldehyde employed, in addition to R% of residue (based on CD). Hydrogenation of the end product analogously to Example 1 gives A₃% of theory of trimethylolpropane (TMP), based on n-butanol.

TABLE

Example	K	T°C	A ₁ % CD	A ₂ % DMB	R %	A ₃ % TMP	Process
1	Dimethylaminoneopentanol	75-80	84.5	80.3	1.6	74.3	Example 1
2	Triethylamine (20 parts)	75-80	85	67	18.8	57	analogously to Example 1
3	Triethylamine	80	79	63	20	51	U.S. Patent 3,077,500 Example 9

EXAMPLE 4

34 parts of triisobutylamine are run into a mixture of 488 parts of 37 per cent strength by weight formaldehyde and 144 parts of n-butyraldehyde in the course of 10 minutes whilst stirring at from 20 to 70°C. The reaction mixture is then stirred for a further 40 minutes at 78°C under reflux. Distillation and hydrogenation analogously to Example 1 give 216 parts of crude dimethylolbutanal (81.8% of theory) or 207 parts of pure dimethylolbutanal (78.4% of theory) or 191 parts of trimethylolpropane, corresponding to 71% of theory, based on n-butyraldehyde.

EXAMPLE 5

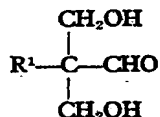
130 parts of dimethylaminoneopentanol are run into a mixture of 1,625 parts of 37 per cent strength by weight formaldehyde and 720 parts of n-butyraldehyde in the course of 15 minutes whilst stirring at from 20 to 80°C. The reaction mixture is then stirred for a further 30 minutes at from 80 to 83°C under reflux. The mixture is distilled using a Sambay evaporator, at 135°C and 10 mm Hg, giving a residue of 909 parts of crude dimethylolbutanal (68.9% of theory) and 1,350 parts of a two-phase distillate. The aqueous phase is brought to pH 8, organic constituents dissolved in the water are distilled off up to a bottom temperature of 100°C, under atmospheric pressure, and the distillate is combined with the organic phase. Fractional distillation of the mixture gives 195 parts of a fraction of boiling range 60—95°C, containing 40 parts of n-butyraldehyde (5.6% by weight of the total starting material) and 150 parts of α -ethylacrolein (17.8% by weight, based on n-butyraldehyde). 190 parts of 37 per cent strength by weight formaldehyde and 25 parts of dimethylamino-neopentanol are added and the mixture is heated at from 60 to 82°C for 5 hours, whilst stirring. After distilling off the low-boiling constituents at 135°C and 10 mm Hg, using a sambay evaporator, 226 parts of crude dimethylolbutanal are obtained as the residue. Total yield: 1,135 parts of dimethylolbutanal, corresponding to 85.5% of theory, based on n-butyraldehyde. Hydrogenation and fractional distillation according to Example 1 give 1,010 parts of trimethylolpropane of boiling point 150—152°C at 1—2 mm Hg (melting point 52°C), corresponding to 75.3% of theory, based on n-butyraldehyde.

EXAMPLE 6

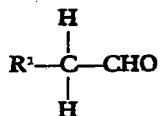
26 parts of dimethylamino-neopentanol are added in the course of 15 minutes to a mixture of 1,220 parts of 37 per cent strength by weight formaldehyde and 290 parts of propionaldehyde whilst stirring at from 20 to 70°C. The reaction mixture is stirred for a further 30 minutes at from 75 to 80°C. The formaldehyde content is lowered to 0.05% by weight (based on the mixture) by stripping with steam and the water and low-boiling constituents are removed by distillation, using a Sambay evaporator at 125°C and 10 mm Hg. 504 parts of crude 2,2-dimethylolpropanal, corresponding to 85.4% of theory, based on propionaldehyde, are left as the residue. Distillation at 140—150°C and 1—2 mm Hg gives 484 parts of dimethylolpropanal of boiling point 125°C at 1—2 mm Hg, corresponding to 82% of theory, based on propionaldehyde. Hydrogenation of the dimethylolpropanal in methanol, analogously to Example 1, gives a solution of 465 parts of trimethylethane. On distilling off the solvent, and recrystallizing the residue from diisopropyl ketone, 454 parts of trimethylethane of melting point 196°C are obtained, corresponding to 75.6% of theory, based on propionaldehyde.

WHAT WE CLAIM IS:—

1. A process for the manufacture of an α,α -dimethylol-substituted aliphatic aldehyde of the formula



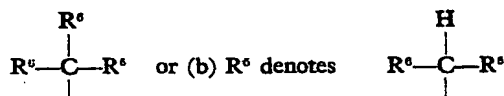
where R^1 is an aliphatic radical, by reaction of an aldehyde with formaldehyde in the presence of a base, wherein an aldehyde of the formula



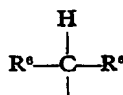
where R^1 has the above meaning, is reacted with formaldehyde in the presence as catalyst of a tertiary amine base of the formula



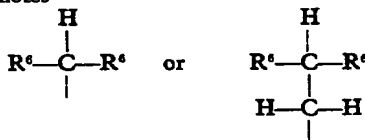
where R^2 and R^3 separately are identical or different aliphatic radicals or together form with the linking nitrogen a heterocyclic ring, and R^4 and R^5 are identical or different aliphatic radicals, and in addition (i) R^4 may denote hydrogen if (a) R^5



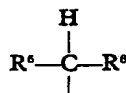
and $R^2 + R^3 +$ the linking N atom form a heterocyclic ring or R^5 denotes



and simultaneously R^2 denotes



and (ii) R^5 may denote hydrogen if (a) $R^2 + R^3 +$ the linking N atom form a heterocyclic ring and R^4 denotes an aliphatic radical or (b) R^4 denotes an aliphatic radical and R^2 denotes



R^5 throughout denoting an aliphatic radical and individual radicals R^4 and individual radicals R^5 being identical or different.

2. A process as claimed in claim 1, wherein the reaction is carried out using from 1 to 8 moles of formaldehyde per mole of starting material II.

3. A process as claimed in claim 1 or 2, wherein the reaction is carried out at from 15 to 120°C.

4. A process as claimed in claim 1 or 2, wherein the reaction is carried out at from 30 to 90°C.

5. A process as claimed in claim 1 or 2, wherein the reaction is carried out at from 40 to 85°C.

6. A process as claimed in any of claims 1 to 5, wherein the reaction is carried out with an aqueous formaldehyde solution of from 20 to 40 per cent strength by weight.

7. A process as claimed in any of claims 1 to 6, wherein the reaction is carried out with an organic, readily water-miscible solvent which is inert under the reaction conditions.

8. A process as claimed in any of claims 1 to 6, wherein the reaction is carried out with from 50 to 1,000% by weight, based on starting material II, of an organic, readily water-miscible solvents which is inert under the reaction conditions.

9. A process as claimed in any of claims 1 to 8, wherein, in the formula of starting material II, R^1 is linear alkyl of 1 to 6 carbon atoms optionally substituted by one or more alkyl or alkoxy groups of 1 to 3 carbon atoms.

10. A process as claimed in any of claims 1 to 9, wherein the reaction is carried out with from 0.03 to 0.15 mole of the catalyst III per mole of starting material II.

11. A process as claimed in any of claims 1 to 9, wherein the reaction is carried out with from 0.05 to 0.1 mole of the catalyst III per mole of starting material II.

12. A process as claimed in any of claims 1 to 11, wherein the reaction is carried out in the presence as catalyst of a tertiary amine as defined in claim 1 in which any aliphatic radical III, where the alkyl of 1 to 7 carbon atoms optionally substituted by one or more dialkylamino groups and/or hydroxyl groups, the alkyl groups of any dialkylamino groups being identical or different and each being of 1 to 5 carbon atoms, and any heterocyclic ring formed by R² and R³ together with the linking nitrogen atom has 5 or 6 ring members, which may include a further nitrogen atom or an oxygen atom and may further be substituted by one or more alkyl or alkoxy groups, in each case of 1 to 3 carbon atoms, dialkylamino groups, in each case of 1 to 3 carbon atoms per alkyl, or hydroxyl groups.

13. A process as claimed in any of claims 1 to 12, wherein the reaction is carried out in the presence as catalyst of dimethylamino-neopentanol, 3-dimethylamino-2-methyl-2-propyl-propanol, 2,2-dimethyl-N,N'-tetramethyl-1,3-propylenediamine, pyrrolidino-neopentanol, 1-dimethylamino-neopentane, 1-dimethylamino-2,2-dimethylolpropane, 1-dimethylamino-2,2-dimethylolbutane, methyl-diisobutylamine, ethyl-diisopropylamine, propyl-diisopropylamine, triisopropylamine, triisobutylamine, propyl-diisobutylamine, n-butyl-diisobutylamine, N-isopropyl-pyrrolidine, N-isobutyl-pyrrolidine, N-isopropyl-piperidine, N-isobutyl-piperidine, methyl-ethylamino-neopentanol, diethylamino-neopentanol, piperidino-neopentanol, 3-(methyl-ethylamino)-2-methyl-2-propyl-propanol, 3-pyrrolidino-2-methyl-2-propyl-propanol, 3-piperidino-2-methyl-2-propyl-propanol, 3-dimethylamino-2-ethyl-2-butyl-propanol, 1-pyrrolidino-2,2-dimethylolpropane, 1-(methyl-ethylamino)-2,2-dimethylolpropane, 1,3-bis-[dimethylamino]neopentane, 1,3-bis-[dimethylamino]-2,2-dimethyl-propanol, methyl-ethylamino-neopentane, ethyl-diisobutylamine, butyl-diisopropylamine, tert-butyl-diisopropylamine, N-isopropylmorpholine, N,N'-diisopropyl-piperazine, N-isobutylmorpholine, N,N'-diisobutyl-piperazine, N-tert-butylpyrrolidine, N-tert-butyl-piperidine or N-tert-butyl morpholine.

14. A process for the manufacture of an α,α -dimethylol-substituted aldehyde carried out substantially as described in any of the foregoing Examples 1 and 4 to 6.

15. α,α -Dimethylol-substituted aliphatic aldehydes when obtained by the process claimed in any of the claims 1 to 14.

16. Trimethylol compounds of the formula R¹-C(CH₂OH)₃ where R¹ has the meaning given in claim 1 or 9, when obtained from α,α -dimethylol-substituted aliphatic aldehydes as claimed in claim 15 by hydrogenation.

17. Polyurethane resins, alkyd resins, drying oil and plasticisers containing trimethylolalkanes as claimed in claim 16.

18. Dimethylolcarboxylic acids when obtained from α,α -dimethylol-substituted aliphatic aldehydes claimed in claim 15.

J. Y. & G. W. JOHNSON,
Furnival House,
14-18 High Holborn,
London WC1V 6DE,
Chartered Patent Agents,
Agents for the Applicants.